

08CNR817-4  
(GP2-0163-P)

## REMARKS

### Nonslauratory Double Patenting Rejection

Claims 1-15 stand rejected under the judicially created doctrine of obviousness-type double patenting as being unpatentable over Claims 1-26 of U.S. Patent No. 6,316,592 to Bates et al. Applicants are submitting herewith a terminal disclaimer in compliance with 37 CFR § 1.321(c) to overcome the rejection.

### Statutory Double Patenting Rejection

Claims 16-27 stand rejected under 35 U.S.C. §101 over claims 15-26 of U.S. Patent No. 6,316,592 to Bates et al. Applicants have canceled Claims 16-27, rendering the rejection moot.

### New Claims

Claims 28-31 have been added to further claim the invention. Claim 28 is supported, at least, by Claim 11 as filed. Claim 29 is supported, at least, by Claim 12 as filed. Claim 30 is supported, at least, by Claims 11 and 14 as filed. Claim 31 is supported, at least, by Claims 11-13 as filed.

08CN8817-4  
(GP2-0163-1)

It is believed that the foregoing amendments and remarks fully comply with the Office Action and that the claims herein should now be allowable to Applicants. Accordingly, reconsideration and allowance is requested.

If there are any additional charges with respect to this Amendment or otherwise, please charge them to Deposit Account No. 07-0862 maintained by Assignee.

Respectfully submitted,

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**(12) United States Patent**  
Bates et al.

**(10) Patent No.:** US 6,316,592 B1  
**(45) Date of Patent:** Nov. 13, 2001

**(51) METHOD FOR ISOLATING POLYMER RESIN FROM SOLUTION SLURRIES**

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**(\*) Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days

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**(22) Filed:** May 4, 2000

**(31) Int. Cl.:** C08J 3/00

**(52) U.S. Cl.:** 528/491; 528/502

**(58) Field of Search:** 524/500; 528/491; 528/502

3,914,366 10/1993 Hay et al. 1,035,541 11/1997 Hay et al. 4,025,451 11/1977 Van Breda et al. 4,077,550 8/1978 Lee et al. 4,108,055 8/1979 Lee, Jr. et al. 4,217,438 8/1980 Baschler et al. 4,517,549 10/1985 Nakamura et al. 4,584,331 8/1986 Lee, Jr. et al. 4,806,297 3/1999 Brown et al. 4,806,302 3/1999 White et al. 4,935,722 6/1990 Brown et al. 4,983,550 \* 11/1991 Blaschke et al. 5,026,591 \* 6/1991 Takada et al. 5,237,005 8/1993 Yates, III et al. 5,453,140 1/1999 Goshikeshi et al. 5,981,554 12/1999 McGuinness et al.

**U.S. PATENT DOCUMENTS**

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**FOREIGN PATENT DOCUMENTS**

0,000,550 A1 2/1981 (DE) 0,111,510 A2 2/1991 (DE) 2,374,614 8/1978 (FR) 1,332,947 9/1973 (DE).

\* cited by examiner

*Primary Examiner:* Paul R. Macht

**(57) ABSTRACT**

Soluble polymer resins are separated from a solution slurry with the use of a precipitation aid where the slurry contains the polymer resin in both a soluble form and a solid particulate phase. The precipitation aid absorbs onto the surface of the solid polymer resin particulates and is a soluble blend component for formation of the polymer resin. The solution slurry may be concentrated and heated prior to precipitation of the polymer resin.

26 Claims, No Drawings

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## METHOD FOR ISOLATING POLYMER RESIN FROM SOLUTION SLURRIES

## BACKGROUND OF THE INVENTION

## 1. Field of the Invention

This invention relates to methods for isolating polymer resin from solution slurries utilizing a precipitation aid.

## 2. Brief Description of Related Art

A number of methods have been disclosed for separating soluble thermoplastic resins from organic solvents. A majority of these methods are energy intensive requiring the removal of the organic solvent. More energy efficient means involve the precipitation or coprecipitation of the polymer resin from solution. These precipitation techniques can be hindered by the presence of a solid phase of fine particulates within the solution. These fine particulates are not easily recovered before precipitation of the soluble polymer resin and can interfere with the recovery of the precipitate. The presence of this solid particulate phase is particularly troublesome when attempting to employ equipment which is not adapted to handle fine particulates.

An example where this problem occurs is in the copolymerization of 2,6-xylenol and 2,3,5-trimethylphenol via oxidative coupling. It is reported that most of the copolymers formed from these monomers spontaneously precipitate in the reaction mixture as very fine particulates. This reaction mixture turns into a three-phase slurry comprising a solid phase of copolymer particulates, a copolymer colloid phase and an aqueous phase. In the preparation of polyphenoxy ether homopolymers with 2,6-xylenol, the polymer reaction product remains soluble in the nitrobenzene reaction solution. After purification of the solution, the homopolymer is typically precipitated in methanol. The polyphenoxy ether homopolymer of 2,6-xylenol precipitates as large size clusters soluble for liquid-solid filtration. In contrast, the three-phase reaction mixture obtained with the preparation of polyphenoxy ether copolymers of 2,6-xylenol and 2,3,5-trimethylphenol is unsuitable for the polymer purification and isolation techniques used for the polyphenoxy ether homopolymers of 2,6-xylenol. Separate equipment is therefore required.

It is desirable to provide an insoluble technique for polymer resins within a solution slurry that contains a solid phase of the polymer resin as fine particulates which does not require special equipment to remove these particulates.

## SUMMARY OF THE INVENTION

This invention provides a method for separating soluble polymer resin from a solution slurry that contains a solid phase of solid polymer resin as particulates. This method comprises adding a precipitation aid to a solution slurry which contains a soluble polymer resin and a solid phase of said polymer resin as particulates. The precipitation aid is a linear or branched polymer which absorbs onto the surface of the polymer resin particulates. This polymeric precipitation aid is also a soluble blend component for formulations of the polymer resin to be isolated.

Following the addition of the precipitation aid, the solution slurry is added to a non-solvent for the soluble polymer resin to precipitate the soluble polymer resin in the solution slurry.

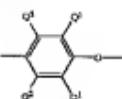
Following precipitation of the soluble polymer resin, it can be recovered by conventional techniques such as by conventional filtration techniques.

The polymer resins which can be isolated from a solution slurry by the methods of this invention have a weight

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average molecular weight of above about 500 as determined by differential scanning calorimetry. Soluble polymer resins include amorphous resins, i.e., polymers which become plastic and flowable under the action of pressure and heat. Specific examples of suitable thermoplastic resins which can be isolated by the methods of this invention are polycarbonates, polystyrenes, high impact polystyrenes, polyphenylene ethers, polyetherimides, polyamides, polymers including polyphenylene sulfonephthalimides and polyphenylene ether isophthalimides. The polymer resins suitable for use in this invention include both homopolymers and copolymers of these thermoplastic resins. The preferred thermoplastic resins employed in the methods of this invention are temperature sensitive polymer resins such as polyphenoxy ether resins.

The polyphenoxy ether resins suitable for use in the methods of this invention are typically prepared in solution by the oxidative coupling of at least one monohydroxy aromatic compound in the presence of a copper, manganese, or nickel catalyst. These polyphenoxy ether polymers comprise a plurality of oxyethylene repeating units preferably with at least 50 repeating units of the following Formula I:



wherein in each of said units independently, each Q<sup>1</sup> is independently halogen, alkyl (preferably primary or secondary, or more preferably primary or secondary lower alkyl up to 7 carbon atoms), alkyl (preferably phenyl), haloalkylcarboxyl group (preferably haloalkyl) having at least two carbons between the halogen atoms and the phenyl nucleus of Formula I, methoxyl, hydroxymethoxy or haloalkyloxymethoxy wherein at least two carbon atoms separate the halogen and oxygen atoms and at least two carbon atoms separate the phenyl nucleus of Formula I.

Each Q<sup>2</sup> is independently hydrogen, halogen, alkyl (preferably primary or secondary lower alkyl up to 7 carbon atoms), alkyl (preferably phenyl), alkylhydrocarbon (preferably haloalkyl) having at least two carbon atoms between the halogen atoms and the phenyl nucleus of Formula I, hydroxymethoxy group or haloalkyloxymethoxy group wherein at least two carbon atoms separate the halogen atoms from the phenyl nucleus of Formula I. Each of Q<sup>1</sup> and Q<sup>2</sup> can similarly contain up to about 12 carbon atoms and most often, each Q<sup>1</sup> is an alkyl or phenyl, especially C<sub>1</sub>-C<sub>6</sub> alkyl and each Q<sup>2</sup> is hydrogen.

The term "polyphenoxy ether resin," as used in the specifications and claims herein, includes: unsaturated polyphenoxy ether polymers; substituted polyphenoxy ether polymers, wherein the aromatic ring is substituted; polyphenoxy ether copolymers; polyphenoxy ether graft polymers containing grafted units such as vinyl acetate, polystyrene, and ethylene;

polyphenoxy ether coupled polymers, wherein coupling agents, e.g., polyisobutene, form high molecular weight polymers and

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end-capped polyphenylene ether polymers with functional end groups.

It will be apparent to those skilled in the art from the foregoing that the polyphenylene ether polymers contemplated for use in the methods of the present invention include all of those previously known, irrespective of the variations in structural units.

Specific polyphenylene ether polymers which can be used in the methods of the present invention include, but are not limited to:

poly(2,6-dimethyl-1,4-phenylene ether);  
 poly(2,6-trimethyl-1,4-phenylene ether);  
 poly(2,6-diethyl-1,4-phenylene ether);  
 poly(2-methyl-5,6-propyl-1,4-phenylene ether);  
 poly(2,6-diisopropyl-1,4-phenylene ether);  
 poly(2-ethyl-5-propyl-1,4-phenylene ether);  
 poly(2,6-diethyl-1,4-phenylene ether);  
 poly(2,6-diphenyl-1,4-phenylene ether);  
 poly(2,6-dimethoxy-1,4-phenylene ether);  
 poly(2,6-diethoxy-1,4-phenylene ether);  
 poly(2-nitroxy-6-ethoxy-1,4-phenylene ether);  
 poly(2-ethyl-6-oxaaryloxy-1,4-phenylene ether);  
 poly(2,6-dichloro-1,4-phenylene ether);  
 poly(2-methyl-6-phenyl-1,4-phenylene ether);  
 poly(2-ethoxy-1,4-phenylene ether);  
 poly(2-ethyl-1,4-phenylene ether);  
 poly(2,6-dimino-1,4-phenylene ether);  
 poly(3-methoxy-2,6-dimethyl-1,4-phenylene ether);  
 the like.

The methods of this invention provide effective results with polyphenylene ether resins which are copolymers of 2,6-dimethyl-1,4-phenylene ether units (from 2,6-xylenol) and 2,6-diisopropyl-1,4-phenylene ether units (from 2,6-trimethylphenol) which typically form fine particulates in the resulting medium.

Specific examples of soluble polyphenylene ether resins and methods for preparing these polyphenylene ether resins are set forth in U.S. Pat. Nos. 3,700,874, 3,806,625, 3,914, 266 and 4,025,711 (Hey); U.S. Pat. Nos. 3,573,857 and 3,257,355 (Sumitomo); U.S. Pat. Nos. 4,535,472 and 4,800,297 (S. B. Brown et al.); and U.S. Pat. No. 4,800,602 (White et al.).

Examples of polymers suitable for use in the methods of this invention are disclosed in U.S. Pat. Nos. 3,961,656 and 5,349,130. Soluble polybutadienes are described in U.S. Pat. Nos. 3,803,085 and 3,905,942. Soluble polyesters include polyethylene terephthalate and poly(ethylene terephthalate and 1,4-dihydroxybutane) as taught in U.S. Pat. No. 5,237,003. Soluble polyurethane are described in U.S. Pat. No. 6,217,438.

The polyacrylate resins suitable for use in this invention include homopolyacrylate, poly(allyl-methacrylate), poly(chloroacrylene) and styrene copolymers with styrene-acrylonitrile copolymers (SAN), acrylate-styrene-acrylonitrile copolymer (ASA), acrylonitrile-butadiene-styrene copolymer (ABS), styrene-maleic anhydride copolymer, styrene-ethylvinylbenzoate copolymer and styrene-dimethylterephthalate copolymers.

Soluble rubber-modified polyacrylate resins (referred to herein as high impact polyacrylate or "HIPS") comprise block and graft HIPS polymer with elastomeric polymers such as polybutadiene.

An important feature of this invention is the presence of both polymer resin particulates as a solid phase and polymer

resin solubilized within the solvent of the solution slurry. While the solid polymer resin particulates phase can interfere with the solubility of the solubilized polymer resin from the solution slurry in conventional techniques, these polymer resin particles take part in the recovery of soluble polymer resin from the solution slurry in this invention.

The solid polymer resin particulates within the solution slurry can be of any size; however, it is important to utilize solids of a size that can be removed easily by conventional filtration techniques. This invention provides advantage with solution slurries that contain solids of an average particle size in the range of from 10 to 75 microns. Preferred solution slurries for the reaction media of solution polymerization processes that contain the polymer resin product in a solid phase (particulates) and a soluble (solvent) phase. An example of such a reaction medium is that of polyphenylene ether resins dissolved in tetrahydrofuran, more particularly, copolymers of 2,6-xylenol (2,6-dimethylphenol) and 2,6-diisopropylphenol in tetrahydrofuran. These slurries typically have particle sizes of below 10 microns.

While the polymer resin particles of the solid phase can vary widely in size, it is preferable that there be some uniformity in size to aid the eventual separation of the polymer resin from the solution slurry.

The concentration of solid polymer resin particulates within the solution slurry can also vary widely and independently less than 70 wt. % based on the weight of a total solution slurry. The methods of this invention can be performed with levels of polymer resin particulates of less than 10%, based on the weight of the total solution slurry. However, it may be possible to ignore the polymer resin solids at such low levels. The use of the methods of this invention at low solid levels such as this is inefficient. Concentrations of polymer resin particulates of from 10 to 60 wt. %, based on the total weight of the slurry are more typical. The reaction media of solution polymerization processes which contain the polymer resin may not have solids at these levels. Therefore, it may be desirable to concentrate the reaction medium to solids levels in this range or at least 10 to 30 wt. %, based on the total weight of the slurry. With higher concentrations of polymer resin particulates, the probability increases that these particulates will interact with the soluble polymer resin and each other.

The solution slurry utilized in this invention contains one or more organic solvents that solubilizes the lower molecular weight species of the polymer resin to provide a soluble polymer resin phase thereof. Examples of suitable solvents for the solution slurry include chlorinated and brominated hydrocarbons having from 1 to 20 carbon atoms such as methylene chloride, 1,1,2,2-tetrachloroethane, 1,2-dichloroethylene, chlorobenzene, chloroform, dichloroethane, 1,1,2-trichloroethane and aromatic and aliphatic hydrocarbons such as benzene, xylene, toluene, pyridine, mesitylene, hexane, pentane, heptane and the like. Mixtures of the above solvents are also suitable. When it is desirable to concentrate the slurry, it is preferable to employ solvents with a boiling point below 100°C. Methylene chloride is a preferred organic solvent for use with polycarbonate resin and toluene is a preferred solvent for both polystyrene and polyphenylene ethers.

The solubilized resin is disengaged from the solid particulate phase by molecular weight. The intrinsic viscosity of the polymer resin which comprises the solid phase can be 2 or 4 times higher than the intrinsic viscosity of the

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solubilized polymer resin. The concentration of soluble resin within the solution slurry can vary widely with amounts up to 60 wt % of the total solution slurry being suitable. Where the solution slurry is a reaction medium of a solution polymerization process that contains polymer resin, the concentration of the polymer resin will depend on the extent of polymerization performed in the reaction medium. Solution slurry vehicles which are the reaction medium of a polyphthalic ester, maleic anhydride, coupling reaction typically have a soluble polyphthalic ester resin at a concentration of about 5 to 25 wt % of the total composition.

In this solution slurry, it is desired to add a solid or shear-bridged polymeric precipitation aid. Thus precipitation aid absorbs onto the surface of the solid resin precipitates of the solid phase, within the solution slurry. Not being bound by theory, it is believed that the polymer chains of the precipitation aid entangle with the precipitation aid that functions as a flocculant. The precipitation aid must be a soluble block copolymer of the first formulation for the polymer resin in that the precipitation aid is not separated from the polymer resin recovered. Suitable polymeric precipitation aids will depend on the polymer resin to be isolated since this precipitation aid must be compatible with the polymer resin in the final formulation. With respect to polyacetates, suitable polymerization aids include impact modifiers as well as polyesters (polybutylenes-trimellitides) and polyimides. For polyphthalic ester resins, suitable precipitation aids include impact modifiers, polyacetates as described above, and polyimides. Impact modifiers also provide suitable precipitation aids for polyacetates, polyetherimides, polyimides, and polyesters in that these resins are typically formulated with impact modifiers when providing suitable articles.

Suitable impact modifiers which can function as a precipitating aid include natural rubbers, synthetic rubbers and thermoplastic elastomers.

Suitable thermoplastic elastomers are homopolymers and copolymers of monomers selected from the group consisting of olefins (e.g., ethylene, propylene, 1-butene, 4-methyl-1-pentene), styrene, alpha-methyl styrene, conjugated dienes (e.g., butadiene, isoprene and chloroprene), vinylidene halides (e.g., acrylic acid and methacrylic acid) and derivatives (e.g., vinylidene carboxylic acids (e.g., vinylidene acetic, allylbenzyl, methyl methacrylate acrylonitrile). Suitable copolymers include random, block and graft copolymers of these monomers described more particularly below.

Specific examples of suitable olefin homopolymers that can be used as a precipitation aid include polyethylene, polypropylene and polybutylenes. The polybutylenes homopolymers include LLDPE (linear low density polyethylene), HDPE (high density polyethylene), MDPE (medium density polyethylene) and isotactic polypropylene. Polyolefin resins of this general structure and methods for their preparation are well known in the art and are described for example in U.S. Pat. Nos. 2,933,680, 3,093,621, 3,211,209, 3,446,168, 3,750,319, 3,854,993, 3,894,999, 4,059,634, 4,166,055 and 4,564,334.

Copolymers of polyolefins may also be used as precipitating aids including copolymers of ethylene and alpha olefins (propylene and 4-methylpentene-1) and EPDM copolymer (copolymer of ethylene, C<sub>4</sub>-C<sub>10</sub> monofunctional and non-conjugated dienes).

Specific examples of conjugated diene homopolymers and random copolymers that can be used as precipitation aids include polybutadiene, butadiene-styrene copolymers, butadiene-acrylate copolymers, isoprene-isobutene acrypolymers, chlorobutadiene polymers, butadiene acrylonitrile polymers and polyacrylates.

Particularly useful precipitation aids are the styrene polymers, preferably styrene block copolymers with conjugated dienes. These include the AB (di-block), A(B)<sub>n</sub>B (tri-block) and ABA (tri-block) block copolymers where blocks A and A' are typically styrene or a similar alkene styrene unit and block B is typically a conjugated diene unit. For block copolymers of formula (AB)<sub>n</sub>B, Integer n is at least 2 and B is a multifunctional coupling agent for the blocks of the structure AB. Suitable conjugated diene blocks include the conjugated diene homopolymers and copolymers described above which may be partially or entirely hydrogenated. The soluble alkene aromatics other than styrene include alpha-methyl styrene, propyl-methyl styrene, vinyl toluene, vinyl styrene and vinyl naphthalene. Examples of triblock copolymers of this type are polyacrylate-polybutadiene-polyacrylate (SBS), hydrogenated polyacrylate-polybutadiene-polyacrylate, styrene-ethylene-butylene styrene (SEBS), polyacrylate-polybutadiene-polyacrylate (SIS) and poly(alpha-methylstyrene)-polyisoprene-poly(alpha-methylstyrene). Examples of commercially available triblock copolymers are the CARGILEX<sup>®</sup>, KRATON<sup>®</sup> and KRATON<sup>®</sup> OG series from Shell Chemical Company.

Also suitable as precipitation aids are Impact modifiers comprising a radial block copolymer of a vinyl aromatic monomer and a conjugated diene monomer. Copolymers of this type generally comprise about 60 to 95 wt % polymerized styrene or similar vinyl aromatic monomer and about 10 to 5 wt % polymerized conjugated diene monomer. The copolymer has at least three polymer chains which form a radial configuration. Each chain terminates in an satisfactorily monosteric segment, to which the elastic polymer segment is joined. These block copolymers are sometimes referred to as "branched" polymers as described in U.S. Pat. No. 4,209,520.

The preferred precipitation aid for a given polymer resin will be determined not only by the degree in which the precipitation aid absorbs onto the surface of the solid resin precipitates, but also by the precipitation aids role in the final formulation of the polymer resin. Impact modifiers and other polymer resins are often used in significant amounts in engineering thermoplastic resin formulations. Use of these materials as precipitation aids will place fewer restrictions on the final formulation. For the impact modifiers, styrene copolymers, particularly ABA block copolymers containing styrene units and conjugated diene units or hydrogenated diene units (ethylene-butylene units) are effective precipitation aids for polyphthalic ester which include copolymers of 2,3,6-trimethylphenol and 2,6-xylenol. Amounts of precipitation aid in the range of 0.5 wt % to 10 wt %, based on the weight of the total solids within the reaction medium (polyphthalic ester and precipitation aid) have been shown to be effective. In a preferred embodiment, the styrene copolymer is a styrene-ethylene-butylene-styrene block copolymer such as those of KRATON<sup>®</sup> OG series available from Shell Chemical Company.

The precipitation aid may be added as a solid that is dispersed in the solution slurry or it may be added in the form of a solution. Adding a precipitation aid to the solution slurry can be accomplished by adding conventional equipment.

Once the precipitation aid has been added to the solution slurry, an optional procedure is to concentrate the solution slurry before precipitation of the resin is initiated. Preferred concentrations for the resin within the solution slurry will vary depending on the particular resin. For polyphthalic ester solutions, resin concentrations in the range of 10 to

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45% are preferred. In crosslinking the solution slurry, it is preferable to heat the solution slurry with or without the application of vacuum. Methods consistent with those described in U.S. Pat. No. 4,992,652 can be used. Applying vacuum will help concentrate the formulation.

Leaving the slurry has been found to enhance the absorption activity of the precipitating aid onto the solid resin particulates. Temperatures in the range of 50° C. and above will provide effective results. Upper temperature limits will be dependent on the thermal sensitivity of the polymer resin, as well as the loss in efficiency of the method employed. For polyphenylene ether resins, temperatures in the range of 60° C. to 115° C. have been found to be effective in enhancing the absorption of a precipitating aid in the polymer resin particulates.

Following the addition of the precipitation aid, the solution slurry is added to a non-solvent for the soluble polymer resin therein so as to precipitate the soluble polymer resin. The term "non-solvent" as used herein intends to refer to solvents that provide a lower solubility for the polymer resin than the solvent of said solution slurry. For a reaction medium of a solution polymerization process that contains polyphenylene ether polymer products and insoluble solvent, methanol is a preferred non-solvent. This is also the case where the polyphenylene ether polymer is an copolymer 2,6-nonyl and 2,3,6-trimethylbenzyl. When the solution slurry has been heated to enhance the absorption of the precipitation aid to the solid polymer resin particulates, it is preferable to quench this heated solution slurry with the non-solvent to stop the agglomeration process. The amount of non-solvent employed is typically from 1 to 4 times the volume of the solution slurry. After the addition of non-solvent, the solution slurry may be agitated if desired. The polymer resin precipitate within the solution slurry may be recovered by conventional means such as through the use of a filter, with or without filter paper. Preferably, the polymer resin is recovered as particles of an average particle size greater than 100 microns to permit the use of filters and/or filter paper having pores of a size above 20 microns, preferably above 50 microns and most preferably above 100 microns. With the increase in pore size, the speed of filtration is increased. Preferably over 90%, more preferably over 95%, of the polymer resin is recovered from the solution slurry by precipitation as solids with a particle size greater than 100 microns.

Although a portion of the particles recovered contain the precipitation aid, it has been found that the resins retain their glass transition temperature, as is evidenced by the differential scanning calorimetry.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

The entire disclosure of all applications, patents and publications, cited above are hereby incorporated by reference.

## EXAMPLES

## Formation Of Solution Slurry

Copolymerization of 2,6-nonyl and 2,3,6-trimethylbenzyl by oxidative coupling was performed in toluene on a pilot plant scale in a 50 gal reactor. The total monomer charge was 52 lbs. Of the total monomer charge, 50 wt % was 2,3,6-trimethylbenzyl. 330 lbs of solvent was

also added that made the total monomer charge about 14 wt % of the reaction medium. A copper/benzene catalyst: Carbonylmethylene diisobutyl ether diisobutyl ether (DIBEDA) 1:1.5, was used at a level which provided a Cuphene ratio of 1:300. After 5 hours of reaction, the catalyst was neutralized and removed. The final reaction contains 11% of soluble polymer based on total monomer charge.

## Examples 1-8

Samples (20g) of the solution slurry described above were mixed with acryne-ethylene butyl acrylate (SEBS) block copolymer sold under the trade name KITAFON-NEXX 1702, available from Shell Chemical Co. The amount of SEBS block copolymer employed in each example is given in Table 1. Selected solution slurries were pre-concentrated in either a 60° C. vacuum oven or 115° C. oil bath, as specified in Table 1. The solids concentration of the solution slurry at the time of precipitation is given in Table 1 as wt %, based on the weight of the total slurry. The solution slurries were then precipitated into 2.5 times of their volume (about 50 ml) of agitated methanol at either room temperature or 50° C., as indicated in Table 1. The precipitated material was vacuum filtered using a "Fritted Buchner Funnel" (nitkile pore size 10-15 microm).

The time of filtration is used as the scaling standard for prior art desirable particulates and these values are reported in Table 1. Because not all of the pre-concentrated material could be transferred into methanol, the "filtration rate" is reported in Table 1 for each example. Filtration rate is the filtration time divided by the weight of final dry material obtained. The data shows rapid filtration times and filtration rates under all conditions, even without pre-concentration as compared to the Comparative Examples Y and Z. Pre-concentration enhanced the filtration time and rate and pre-concentration at higher temperatures (115° C.) improved these values even further. Using less than 10 wt % SEBS copolymer shows 50 seconds and most preferably above 100 seconds. With the increase in pore size, the speed of filtration is increased. Preferably over 90%, more preferably over 95%, of the polymer resin is recovered from the solution slurry by precipitation as solids with a particle size greater than 100 microns.

## Comparative Examples Y and Z

For comparison purposes, 20 g samples of the solution slurry prepared above were pre-concentrated as indicated in Table 1 and precipitated in agitated methanol, as described in Examples 1-8. The solution slurries of the comparative examples were not precipitated with the precipitation aid, SEBS rubber. The comparative examples required significantly longer filtration times and higher filtration rates. The filtration times of Comparative Examples Y and Z are eight times longer than the filtration times of Examples 1-8, which was pre-concentrated and precipitated under similar conditions. The difference in the filtration rates is even longer. The filtration time of Comparative Example Z is about 9 times greater than the filtration time for Examples 1-8, which was pre-concentrated and precipitated under similar conditions.

TABLE I

	Expt.	SEBS wt %	SEBS (wt %)	Conc. (wt %)	Multi- -wt (%)	Filtration Time (Sec.)	Filtration Rate (Sec.)
1	152	10.0	NA	NA	60	21	
2	182	10.0	NA	50	60	39	
3	187	10.0	51 + vacuum	51	20	18	
4	120	10.0	51 + vacuum	50	18	6.1	
5	144	10.0	51	51	14	8.2	
6	135	10.0	51	51	15	3.6	

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TABLE I-continued

Experi- ment no.	Styrene (wt %) (g)	Butyl phenol (g)	Cross- linked polymer (g)	Monomer (g)	Styrene (g)	Styrene (g)	Styrene (g)
7	18.6	9.0	115	30	25	8.0	5
8	18.6	9.0	115	30	25	8.0	5
9	21.2	9.0	55 + precipitate	50	400	25.0	10
7	21.6	9	115	50	81	8.2	10

## Example 9-10 and Comparative Example X

Another solution slurry comprising a copolymer of 2,6-xylenol and 2,3,6-trimethylphenol was prepared by oxidative coupling in solution on a pilot plant scale as described above. The catalyst was removed from the solution slurry before precipitation.

Samples of this solution slurry (about 100 g) with catalyst removed were mixed with about 30% v/v 96-98% KUATUN99 GX-1702 styrene ethylene butylene styrene block copolymer available from Shell Chemical Co. Two solution slurries, A and B, were tested in Examples 9, both having about 5.04 wt % SEBS block copolymer. Three solution slurries, A, B and C, were tested in Example 10. The amounts of SEBS block copolymer employed in the solution slurry of Examples 9 and 10 are reported in Table 2. Comparative Example X was a solution slurry that did not employ SEBS block copolymer.

Each solution slurry was pre-concentrated in a 115°C oil bath and precipitated into 2.5 times the volume of agitated methanol at room temperature. The precipitated material was then vacuum filtered using a Borelli funnel and filter paper of various pore sizes (20 microns, 50 microns, 100 microns), as indicated in Table 3.

The results show an increase in the yield of the precipitate (filtration yield) with the use of a SEBS block copolymer precipitating aid as compared to Comparative Example X. The results also show that the level of precipitating aid has an effect on the particle size of the precipitate, with high levels of the SEBS block copolymer precipitating aid, filter papers with larger pore sizes (100 microns and 50 microns) can be used while maintaining high yields above 90%, as shown in Table 2.

TABLE II-2

Example #	Forb. Solvent (wt %) (g)	Styrene (wt %) (g)	Styrene (g)	Monomer (g)	Styrene (g)	Styrene (g)	Styrene (g)
Example 9A	19.6	10.0	20	115	9.0	8.0	5
9B	19.6	10.0	50	115	9.0	8.0	5
Example 10A	18.0	9.0	20	55	9.0	8.0	10
10B	18.0	9.0	50	55	9.0	8.0	10
10C	21.6	9	100	55	9.0	9.0	10
Comparative Example X	21	9	30	115	0	0	0

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

What is claimed:

1. A method for separating a soluble polymer resin from a solution slurry, which contains a solid phase of said polymer resin as particulates, said method comprising:

adding to a solution slurry which contains at least one soluble polymer resin selected from the group consist-

ing of polyacrylonitrile, polyacrylates, nitrile modified polyacrylates, polyphenylene ethers, polyetherimides, polyamides, and polyesters and a solid phase of said polymer resin as particulates, a linear or chain branched polystyrene precipitating aid which absorbs onto the surface of the polymer resin particulates in said solution slurry, wherein said precipitating aid is a suitable blend component for formulation of said polymer resin, and

adding the solution slurry, which contains said precipitating aid, to a non-solvent for the soluble polymer resin to precipitate the soluble polymer resin within said solution slurry.

2. A method as in claim 1 comprising the additional step of recovering the precipitate from said solution slurry.

3. A method as in claim 2, wherein the precipitate is recovered from said solution slurry by filtration through a filter having a pore size greater than 100 microns.

4. A method as in claim 2, wherein over 90% of the total polymer resin in said solution slurry, including the soluble polymer resin and the solid phase polymer resin, is recovered as particulates of a size greater than 100 microns.

5. A method as in claim 1, wherein the soluble polymer resin within the solution slurry is a polyphenylene ether resin.

6. A method as in claim 1, wherein the soluble polymer resin within said solution slurry is a copolymer of 2,6-xylenol and 2,3,6-trimethylphenol and the solution slurry is a reaction medium of a solution polymerization process in which said copolymer has been produced.

7. A method as in claim 1, which comprises the additional step of concentrating said solution slurry after the addition of said precipitating aid to achieve a concentration of soluble polymer resin above 10%, based on the total weight of said solution slurry.

8. A method as in claim 7, wherein said solution slurry is concentrated by heating to a temperature above 50°C, optionally with the application of vacuum.

9. A method as in claim 5, wherein the precipitating aid is selected from the group consisting of polyesters, polyacrylates, polyamides, and impact modifiers.

10. A method as in claim 9, wherein the impact modifier is selected from the group consisting of natural rubbers, synthetic rubbers and thermoplastic elastomers selected from the group consisting of olefin homopolymers, olefin copolymers, styrene homopolymers, styrene copolymers, homopolymers of conjugated dienes, copolymers of conjugated dienes, homopolymers of vinyl carboxylic acids, copolymers of vinyl carboxylic acids, homopolymers of derivatives of vinyl carboxylic acids and copolymers of derivatives of vinyl carboxylic acids.

11. A method as in claim 10, wherein the olefin copolymers comprise EPDM copolymers, the conjugated diene homopolymers comprise polybutadiene and the styrene copolymers include ABS, (ABA)-R and ABA block copolymers.

12. A method as in claim 11, wherein the styrene block copolymers comprise styrene-butadiene-styrene block copolymers, styrene-ethylene-butylene-styrene block copolymers, polyacrylate-polystyrene-polystyrene block copolymers, hydrogenated polystyrene-polychlorotoluene-polystyrene block copolymers and poly[ $\alpha$ -methylstyrene]-polystyrene-poly[ $\alpha$ -methylstyrene] block copolymers.

13. A method as in claim 10, wherein the styrene copolymer is a styrene block copolymer.

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14. A method as in claim 3, wherein the amount of precipitation aid added to said solution slurry falls within the range of 1 to 10 wt. %, based on the total weight of soluble polymer resin in said solution slurry.

15. A method for separating a soluble polyphenylene ether resin from a solution slurry, said method comprising:

adding to a solution slurry which contains at least one soluble polyphenylene ether resin and a solid phase of polyphenylene ether resin particulates, a linear or cross-branched polynionic precipitation aid which absorbs onto the surface of the polyphenylene ether particulates within said solution slurry, wherein said precipitation aid is a blend component for the first formulation of said polyphenylene ether resin;

adding the solution slurry, which contains the precipitation aid, to a non-solvent for the soluble polyphenylene ether resin so as to precipitate said soluble polyphenylene ether resin in said solution slurry.

16. A method as in claim 15, comprising the additional step of recovering the precipitate from said solution slurry.

17. A method as in claim 15, wherein the precipitate is recovered from said solution slurry by filtration through a filter having a pore size greater than 100 microns.

18. A method as in claim 15, wherein over 90% of the total polyphenylene ether resin in said solution slurry, including the soluble polyphenylene ether polymer resin and the solid polyphenylene ether polymer resin, is recovered as particles of a size greater than 100 microns.

19. A method as in claim 15, wherein the polyphenylene ether resin within said solution slurry is a copolymer of 2,6-dimethylphenol and 2,3,6-trimethylphenol and the solution slurry is a solution medium of a solution polymerization process which produces said copolymer.

20. A method as in claim 15, which comprises the additional step of concentrating said solution slurry after the addition of said precipitation aid to achieve a concentration of soluble polymer resin above 25%, based on the total weight of said solution slurry.

21. A method as in claim 15, wherein said solution slurry is concentrated by heating to a temperature above 50° C., optionally with the application of vacuum.

22. A method as in claim 15, wherein the precipitation aid is selected from the group consisting of impact modifiers.

23. A method as in claim 22, wherein the impact modifier is selected from the group consisting of thermoplastic elastomers selected from the group consisting of ethylene terpolymers, ethylene copolymers, styrene homopolymers, styrene copolymers, the copolymer of conjugated dienes and copolymers of conjugated dienes.

24. A method as in claim 15, wherein the ethylene copolymer comprising EPDM copolymers, the conjugated diene terpolymers comprising polybutadiene and the styrene copolymers comprising styrene block copolymers.

25. A method as in claim 15, wherein the styrene block copolymers comprise styrene-butadiene-styrene block copolymers, styrene-ethylene-butylene-styrene block copolymers, polystyrene-polymethylstyrene-polystyrene block copolymers, hydrogenated polystyrene-polychlorofluoropolystyrene block copolymers and poly( $\alpha$ -methylstyrene)-polymethylstyrene-poly( $\alpha$ -methylstyrene) copolymers.

26. A method as in claim 15, wherein the amount of precipitation aid added to said solution slurry falls within the range of 1 to 10 wt. %, based on the total weight of soluble polyphenylene ether polymer resin in said solution slurry.

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